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Homogeneities of Trace Amounts of Selenium in Powdered Samples and the Variation of Oxidation-State of the Element During Storage

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A method is described for the preparation of powdered samples containing trace amounts of selenium. In this method, a dried sample was homogenized by quartering four times after the crushing of the sample in an agate mill for 10 minutes. A small amount of zinc selenide was mixed in powdered silica by means of the method, and the homogeneity of selenium in the silica sample was investigated; The homogeneities of 90.4% and 92.4% were obtained in the samples of 10 mg Se/g and 100 μg Se/g, respectively. Furthermore, the variation of oxidation-state of selenium was obtained in the selenide-samples during storage. This sample-preparation method was applied to sediment-samples characterized to each environment of the sedimentations, and the homogeneities of selenium and other trace constituents in the sediments were studied.

KEY WORDS : Sample treatment / Sediment / Fluorometry / Selenium / Homogeneity /

INTRODUCTION

Sampling and the preparation of samples have been a significant field of analytical chemistry in order to grasp the occurrence of elements present in the environment from which the sample was taken. For the determination of trace elements and organic substances in environmental materials such as sediment-, soil- and rock-samples, the preparation of these samples should be done prior to the determination of trace constituents in the materials. Even though a highly accurate sensitive analysis is applied to determine the trace element, it is difficult to obtain a true analytical value of the element because the possibility of a segregation of the constituent will be expected in a certain sample insufficiantly prepared. On the other hand, it has been reported that the oxidation-state of iron is changed to iron(III) from iron(II) during the preparation of rock-samples[1]. Therefore, it is not only a difficult problem but also a basic subject in analytical chemistry and geochemistry to analyze the exact occurrence and oxidation-state of trace elements in environmental powdered materials.

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EXPERIMENTAL

Reagents, samples and apparatus

Standard sample of selenide. Zinc selenide (99.999%, Mitsuwa Kagaku Co. Ltd.) was used.

Silica sample. A quartz cell was crushed and powdered to pass through a sieve of 100 mesh size, washed with hydrochloric acid by the boiling of the powder, and dried, then used as the material to dilute the standard samples of selenide.

Sediment and plant samples. Yodo River sediment was collected from the depth of 10 cm at the Hirakata city (near Hirakata-Ohashi, Osaka pref.)[2]. The Pacific sediment was collected from 6000 m depth at 34°52′N, 151°55′E during the Hakuhomaru KH 75-3 sailing[3]. The Japan Sea sediment was collected from 3160 m depth at 39°01′N, 130°00′E.[3,4] The Suruga Bay sediment was collected from 1450-1550 m depth at off shore of Shimizu city (Shizuoka pref.)[2,5]. All the sediment samples dried in an air-oven at 110°C. The NBS river sediment[6] supplied from NBS was used for the analysis. The plant reference materials, Bamboo grass leaves[7] and Pepperbush leaves[8], prepared by a ballmill were also used after the weights of these samples were constant in a desiccator on silica gel.

Other reagents and apparatus employed are described in the paper[5].

Preparation of samples

A dried sample was crushed and powdered in an agate mill for 10 minutes, and the sample was prepared by quartering four times to homogenize. In order to investigate the homogeneity of selenium and the variation of the oxidation-state of selenide in the silica-selenide sample, the selenide samples No. 1 and No. 2 were manufactured by the sample-preparation method described above. The procedure of the preparation of these two samples was shown in Fig. 1.

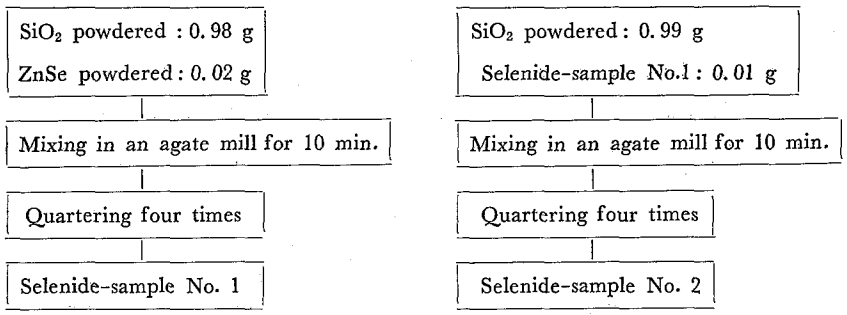

Fig. 1 Flow diagram for the preparation of selenide-samples.

Determination of total amounts of selenium

Total amounts of selenium in sediment samples and plant materials were determined by the fluorimetric method with 2, 3-diaminonaphthalene[5]. Total amounts of selenium in selenide samples were also determined by the method[5], after the chemical pre-

treatment of the samples, as described as follows.

About 10 mg portions of the selenide-sample were taken in a beaker and 3 ml of 0.1N NaOH solution and 2 ml of 30% H_2O_2 solution were added. After boiling the mixture for a few minutes, 5 ml of concentrated nitric acid were added to the beaker and the solution was boiled again. After cooling, the residue was separated with 3 μ membrane filter, and the filtrate was diluted with water to an appropriate volume. To an aliquot taken from the solution, 0.5 ml of 70% $HClO_4$ were added, and dried up to the fumes of $HClO_4$. Selenium in the solution was reduced to selenium(IV) by boiling with 2 ml of 6N HCl for 3 minutes, and selenium(IV) was fluorimetrically determined with 2, 3-diaminonaphthalene[5].

Determination of selenide

A method based on the principle of producing H_2Se[9] was applied to the selenide-sample No. 1 and No. 2 in order to determine selenide in the samples. The procedure of the method was shown as follows. About 10 mg portions of the selenide-sample were transferred to the reaction vessel placed on an aluminium block which was drilled to hold an hole. To the absorbing tube 2.5 ml of 0.1N NaOH and 7.5 ml of 30% H_2O_2 solutions were added, and the tube was connected with the reaction vessel. The separatory funnel was set in the vessel, and 20 ml of 6N HCl were added dropwise with the carrier gas of N_2. The aluminium block was heated at 170°C for 40 minutes. In this method, selenium(0), selenium(IV) and selenium(VI) were scarcely detected in the absorbing vessel.

RESULTS AND DISCUSSION

Homogeneity of selenium in the selenide-samples

Table I shows the analytical results and homogeneity of selenium in the selenide-

Table I. Homogeneity of selenium in the Selenide-Samples No. 1 and No. 2

Selenide-sample No 1			Selenide-sample No. 2		
Se content calculated : 10.3 μg/mg (SiO_2 : 0.9778 g, ZnSe : 0.0188 g)			Se content calculated : 111 μg/g (SiO_2 : 1.0124 g, ZnSe : 0.0110 g)		
Exp. No.	Sample taken (mg)	Se content (μg/mg)	Exp. No.	Sample taken (mg)	Se content (μg/g)
1	8.3	11.4	1	12.8	89.0
2	13.2	10.5	2	11.1	80.4
3	9.2	10.7	3	10.6	90.2
4	10.4	9.29	4	11.1	79.7
5	10.7	9.61	5	12.1	95.1
6	10.6	8.85	6	14.1	94.5
Average±std. dev.		10.1±0.97	Average±std. dev.		88.2±6.7
C. V.		9.6%	C. V.		7.6%
Homogeneity		90.4%	Homogeneity		92.4%

sample No. 1 and No. 2 prepared by the procedure given in Fig. 1. The content of selenium was adjusted with silica powders to contain one percent of selenium in the selenide-samples. On the diluting selenide by mixing zinc selenide with silica powder, the size weight ratio[10] was calculated to be 0.01 because of the 1% of the selenide content. Therefore, the relative standard deviation of selenium will be expected to be 0.1% for the calculated value of selenium content of the selenide-sample ($\sqrt{0.01\times1}=0.1$). On the other hand, analytical precision of selenium was given to be 0.4% for the determination of selenium in the sample with 2, 3-diaminonaphthalene. From the consideration of these values, it was able to be pointed out that the homogeneities of selenium in the selenide-samples No. 1 and No. 2 were estimated to be 90.4% and 92.4%, respectively.

Homogeneities of trace constituents in sediment samples

Four sediment samples were prepared by the proposed method, and the homogeneities of selenium, scandium, cobalt, humic acid and fulvic acid were investigated. The results of the homogeneities of trace constituents in sediments were listed in Table II.

Table II. Homogeneity of Trace Constituents in Sediment Samples

Sample Element or substance determined		Content (ppm) Average ± std. dev.			C.V.(%)	Analytical method	Analytical precision (%)	Homogeneity (%)	Reference
The Yodo River sediment (Depth : 0.1m)	Se	0.301	±0.036	(4)	12	Capric acid chloroform extraction method	2.1	88	2) 11)
	H. A.	9.02	±1.83	(6)	20	Fluorimetric method	2	80	12)
	F. A.	100.0_3	$\pm9.9_5$	(6)	10		0.6	90	12)
The Suruga Bay sediment (Depth : 1450-1550m)	Se	0.474	±0.018	(3)	4	DAN-cyclohexane extraction method	0.4	96	2)
	H. A.	8.2_4	$\pm0.7_8$	(5)	9	Fluorimetric method	2	91	12)
	F. A.	46.1_2	$\pm1.4_3$	(3)	3		0.6	97	12)
The Japan Sea sediment (Depth : 3162m)	H. A.	2.6_0	$\pm0.0_7$	(4)	3	Fluorimetric method	2	97	12)
	F. A.	9.3_0	$\pm0.4_2$	(4)	5		0.6	95	12)
The Pacific sediment (Depth : 6000m)	Sc	25.1	±1.0	(3)	4	Neutron Activation Analysis	0.7	96	5)
		34.9	±2.2	(3)	6.1		0.7	93.9	5)
	Co	35.1	±1.4	(3)	4.0		1	96	5)
		50.4	±3.2	(3)	6.4		2	93.6	5)

H. A. : Humic acid
F. A. : Fulvic acid
( ) ; Number of determinations

By comparing the homogeneities of these trace constituents with geochemical characters of the sediment samples, the following results were obtained.

(1) In the case of selenium, the homogeneity of selenium in each sediment sample was in the range of 88 −96%, and it was found that the result of the homogeneity test in the selenide samples, 90−92%, was included within the range of that in the sediment samples employed for the test.

(2) In the comparison of the homogeneity of selenium with fulvic acid, both of the values of homogeneities were found to be almost equal in each sample, while the homogeneity of humic acid in the same sample was shown to be lower than selenium or fulvic acid. Especially, in the Yodo River sediment, the homogeneity of humic acid was obtained to be 80 per cent. It is an interesting phenomenon that humic acid was indicated to be existed in the river sediment as the condition of much segregation, and might be related with the environment growing with aquatic plants in the Yodo River.

(3) There was a tendency that high homogeneities of trace constituents were found to be in pelagic sediments or deep sea sediments. It seems to be considered that the tendency is associated with the sedimentation rate at the environment which a sampling of sediments is done.

Effects of the methods of sample-preparations on the homogeneity of trace amounts of selenium

For the preparation of samples, the presented method, the other method such as milling with balls and a non-prepared mothod were applied to sediment and plant samples, and the homogeneities of trace amounts of selenium in the samples prepared by these methods were tested. The results of the test were summarized in Table III.

Table III. Homogeneity of Selenium in the Samples of Sediments and Plants

Sample	Method of sample-preparation	Se content (ppm)	Averge±std. dev. (ppm)	C. V. (%)	Homogeneity (%)
NBS river sediment	none	0.530			
	none	0.527			
	none	0.670	0.883±0.425	48	52
	none	1.33			
	none	1.36			
The Japan Sea sediment (Depth: 1000m)	none	3.177			
	proposed method	1.062			
Bamboo grass leaves	ball mill	0.0175			
	ball mill	0.0186	0.0195±0.0026	13	87
	ball mill	0.0224			
Pepper-bush leaves	ball mill	0.129			
	ball mill	0.126	0.123±0.008	6.5	93.5
	ball mill	0.114			

Analytical method of selenium: fluorimentry [3]

In the river sediment supplied from the NBS, the chemical analysis of selenium was carried out without the sample-preparation of the sediment. From the analytical results, *i. e.* 52% as the homogeneity, it was indicated that the high segregation of selenium was observed in the NBS river sediment. On the other hand, the homogeneities of major constituents in the NBS sediment were investigated and found to be good homogenized[6]. This seems to be an interesting experimental result in analytical chemistry and geochemistry, and the subject should be analyzed in further detail. Furthermore, in the

case of the Japan Sea sediment, the selenium content was higher than the other sediments, and was largely varied as the proposed method of sample-preparations was not applied to the sediment. The plant samples, Bamboo grass leaves and Pepperbush leaves, were prepared by a ball-mill, and the homogeneities of selenium in the samples were 87% and 93.5%, respectively. It was found that good homogeneous values were obtained by not only the presented method but also the ball-mill technique.

Variation of oxidation-state of the selenide sample during stoirage

The hydrogen selenide method[9] was applied for the determination of selenide contents of the selenide-samples No. 1 and No. 2 prepared by the procedure given in Fig. 1, and the variation of oxidation-state of selenide during storage was investigated. As shown in Fig. 2, the selenide content tended to decrease after the selenide-sample

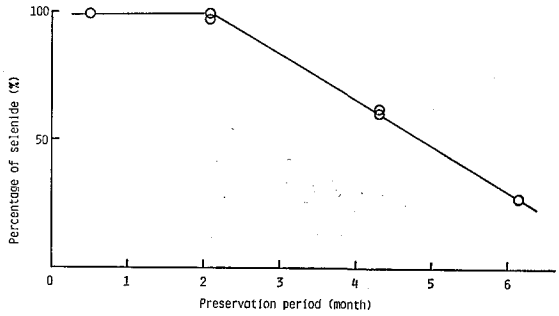

Fig. 2 Variation of the oxidation state of selenium in the selende-sample No. 1 Selenide : 100μg Analytical method of selenide : fluorimetry (H_2Se system) [9]

No. 1 was kept in a desiccator for more than two months. It can be considered from the chemical mechanism of the hydrogen selenide method that the tendency was observed owing to the oxidation of selenium (−II) to selenium(O). In the case of the selenide-sample No. 2, the selenide content was found to be only 15% during the storage within one month. Accordingly, it must be recognized that enough attention should be given to analyze the oxidation-state of low content of selenide samples.

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